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(54) **Process for the preparation of hydrocarbons.**

(57) In the preparation of hydrocarbons from syngas over a Co/Zr/SiO₂ catalyst which has been prepared by impregnation and/or kneading, the catalyst is applied in the form of a fixed bed which meets a specified relation between its external (S_e) and internal (S_i) surface.

In order to show a high C₅⁺ selectivity the catalyst bed should have an S_e (between 5 and 70 cm²/ml) and an S_i (between 10 and 400 m²/ml) such that the following relation is satisfied:

$$10^6 > S_e^2 \times S_i > 2.5 \times 10^4.$$

PROCESS FOR THE PREPARATION OF HYDROCARBONS

The invention relates to a process for the preparation of hydrocarbons by catalytic reaction of carbon monoxide with hydrogen.

The preparation of hydrocarbons from an H_2/CO mixture by
5 contacting this mixture at elevated temperature and pressure with
a catalyst is known in the literature as the Fischer-Tropsch
hydrocarbon synthesis process. Catalysts frequently used for this
purpose contain one or more metals of the iron group together with
one or more promoters and a carrier. For the preparation of these
10 catalysts the known preparation techniques such as precipitation,
impregnation, kneading and smelting are suitable. The products
which can be prepared with these catalysts usually possess a very
wide molecular weight distribution and in addition to branched and
unbranched paraffins often contain considerable quantities of
15 olefins and oxygen-containing organic compounds. As a rule only a
minor portion of the resultant products consists of middle
distillates. Besides the yield, the pour point of these middle
distillates also leaves something to be desired. In view of this,
the direct conversion of H_2/CO mixtures by the Fischer-Tropsch
20 process is not a particularly attractive route for the preparation
of middle distillates on the technical scale.

In this patent application, the term "middle distillates" is
understood as hydrocarbon mixtures having a boiling range
principally corresponding to that of the kerosine and gas oil
25 fractions which are obtained in the conventional atmospheric
distillation of crude petroleum. The middle distillate range
extends principally between approx. 150 and 360 °C.

Recently a class of Fischer-Tropsch catalysts was discovered
which possess the property of yielding a product containing only
30 very few olefins and oxygen-containing organic compounds and

consisting virtually completely of unbranched paraffins a substantial proportion of which have a boiling point above the middle distillate range. It has been found that the high-boiling portion of this product can be converted at high yield into middle distillates by means of hydrocracking. The feedstock chosen for the hydrocracking treatment is at least that portion of the product of which the initial boiling point is above the final boiling point of the heaviest middle distillate desired as end product. The hydrocracking treatment, which features a very low hydrogen consumption, yields middle distillates with a considerably better pour point than those obtained in the direct conversion of an H_2/CO mixture by the Fischer-Tropsch process.

The Fischer-Tropsch catalysts belonging to the above-mentioned class contain silica, alumina or silica-alumina as carrier and cobalt together with zirconium, titanium and/or chromium as catalytically active metals in such proportions that the catalysts contain 3-60 parts by weight of cobalt and 0.1-100 parts by weight of zirconium, titanium and/or chromium per 100 parts by weight of carrier. The catalysts are prepared by applying the metals concerned to the carrier by means of kneading and/or impregnation. For further information concerning the preparation of these catalysts by kneading and/or impregnation reference is made to the Netherlands patent application No. 8301922 recently filed in the name of the Applicant.

A further investigation into the use of above-mentioned cobalt catalysts in the form of a fixed bed has now disclosed that their performance in terms of C_5^+ selectivity is in large measure dependent on the external and internal surface area of the catalyst bed.

It has been found that an optimum performance in terms of C_5^+ selectivity can be obtained if the catalyst has an external surface area (S_e) between 5 and 70 cm^2/ml and an internal surface area (S_i) between 10 and 400 m^2/ml such as to satisfy the relationship $10^6 > S_e^2 \times S_i > 2.5 \times 10^4$.

The present patent application therefore relates to a process for the preparation of hydrocarbons by catalytic reaction of carbon monoxide with hydrogen, in which a mixture of carbon monoxide and hydrogen is contacted at elevated temperature and pressure with a catalyst which contains 3-60 parts by weight of cobalt and 0.1-100 parts by weight of at least one other metal selected from zirconium, titanium and chromium per 100 parts by weight of silica, alumina or silica-alumina, and which catalyst is prepared by kneading and/or impregnation, the catalyst being present in the form of a fixed bed and the catalyst bed having an external surface area (S_e) between 5 and 70 cm^2/ml and an internal surface area (S_i) between 10 and 400 m^2/ml such as to satisfy the relationship $10^6 > S_e^2 \times S_i > 2.5 \times 10^4$.

The external surface area (S_e) of the catalyst bed can be found for a representative sample with a given volume expressed in ml by determining the external surface area expressed in cm^2 of each of the catalyst particles present therein, summing the external surface areas found and dividing the sum by the volume of the sample. The internal surface area S_i of the catalyst bed is determined by means of nitrogen adsorption.

In the process according to the invention, use is preferentially made of the cobalt catalysts which are the subject of the Netherlands patent application No. 8301922. These are catalysts which satisfy the relationship

$$(3 + 4 R) > \frac{L}{S_i} > (0.3 + 0.4 R), \text{ wherein}$$

L = the total quantity of cobalt present on the catalyst, expressed in mg of Co/ml,

S_i = the internal surface area of the catalyst, expressed in m^2/ml , and

R = the weight ratio between the quantity of cobalt applied to the catalyst by kneading and the total quantity of cobalt present on the catalyst.

In the process according to the invention, preferential use is further made of cobalt catalysts prepared by any one of the three following procedures:

- a) cobalt is first applied by impregnation in one or more steps and subsequently the other metal is likewise applied by impregnation in one or more steps,
- b) the other metal is first applied by impregnation in one or more steps and subsequently cobalt is likewise applied by impregnation in one or more steps, and
- c) cobalt is first applied by kneading in one or more steps and subsequently the other metal is applied by impregnation in one or more steps.

In the process according to the invention, preferential use is further made of cobalt catalysts containing 15-50 parts by weight of cobalt per 100 parts by weight of carrier. The quantity of the other metal preferentially present in the cobalt catalysts depends on the manner in which this metal is applied. In the case of catalysts where first the cobalt and then the other metal is applied to the carrier, preference is given to catalysts containing 0.1-5 parts by weight of the other metal per 100 parts by weight of carrier. In the case of catalysts where first the other metal and then the cobalt is applied to the carrier, preference is given to catalysts containing from 5 to 40 parts by weight of the other metal per 100 parts by weight of carrier. For the other metal it is preferred to use zirconium and for the carrier it is preferred to use silica.

According to the invention, in order to achieve optimum performance in terms of C_5^+ selectivity, the S_e and S_i of the catalyst bed must satisfy the following requirements:

$$\begin{aligned}
 S_e &= 5-70 \text{ cm}^2/\text{ml} \\
 S_i &= 10-400 \text{ m}^2/\text{ml}, \text{ and} \\
 10^6 &> S_e^2 \times S_i > 2.5 \times 10^4.
 \end{aligned}$$

It is preferred to use a catalyst bed which satisfies:

$$S_e = 10-50 \text{ cm}^3/\text{ml},$$

$$S_i = 15-200 \text{ m}^2/\text{ml}, \text{ and}$$

$$2.5 \times 10^5 > S_e^2 \times S_i > 3 \times 10^4.$$

5 Before becoming suitable for utilization in the preparation of hydrocarbons from an H_2/CO mixture, the cobalt catalysts have to be activated. This activation can suitably be carried out by contacting the catalysts at a temperature between 200 and 350 °C with hydrogen or a hydrogen-containing gas.

10 The conversion of the H_2/CO mixture into hydrocarbons according to the invention is preferentially carried out at a temperature of 125 to 350 °C, and in particular of 175 to 275 °C, and a pressure of 5 to 500 bar, in particular of 10 to 75 bar.

15 H_2/CO mixtures which are suitable for conversion according to the invention into hydrocarbons can be very suitably obtained starting from light hydrocarbons such as methane by means of steam reforming or partial oxidation. Special preference is given to the use of natural gas as feedstock for the preparation of the H_2/CO mixture.

20 The H_2/CO mixture converted according to the invention into hydrocarbons preferentially possesses an H_2/CO molar ratio of more than 1.5. If the feedstock possesses an H_2/CO molar ratio of less than 1.5, it is preferentially raised to a value between 1.5 and 2.5 and in particular to a value between 1.75 and 2.25 before
25 being contacted with the cobalt catalyst. Raising of the H_2/CO molar ratio of hydrogen-lean H_2/CO mixtures can be performed, inter alia, by the addition of hydrogen, removal of carbon monoxide, admixture of a hydrogen-rich H_2/CO mixture or by applying the CO shift reaction to the hydrogen-lean H_2/CO mixture.

30 As has already been mentioned above, when used for the conversion of an H_2/CO mixture the present cobalt catalysts yield a substantially paraffinic product of which the high-boiling portion can be converted at high yield into middle distillates by means of a hydrocracking treatment. The feedstock chosen for the

hydrocracking treatment is at least that portion of the product of which the initial boiling point is above the final boiling point of the heaviest middle distillate desired as end product.

Although in the preparation of middle distillates the product
5 obtained over the cobalt catalyst it is sufficient to use as feedstock for the hydrocracking treatment that portion of the product of which the initial boiling point is above the final boiling point of the heaviest middle distillate desired as end product, for this purpose it is preferred to use the total C_5^+
10 fraction of the product prepared over the cobalt catalyst because it has been found that under the influence of the catalytic hydrogen treatment a quality improvement takes place in the gasoline, kerosine and gas oil fractions present therein.

The hydrocracking treatment is carried out by contacting the
15 fraction to be treated, at elevated temperature and pressure and in the presence of hydrogen, with a catalyst containing one or more noble metals of Group VIII on a carrier. The hydrocracking catalyst used is preferentially a catalyst containing 0.1-2% by weight and in particular 0.2-1% by weight of one or more noble
20 metals of Group VIII on a carrier. Preference is given to catalysts containing as Group VIII noble metal platinum or palladium, and silica-alumina as carrier. The hydrocracking treatment is preferentially carried out at a temperature of 200-400°C and in particular of 250-350 °C and a pressure of 5-200
25 bar and in particular of 10-75 bar.

The invention will now be elucidated with reference to the following Example.

EXAMPLE

Nine Co/Zr/SiO₂ catalysts (catalysts 1-9) were prepared by
30 impregnation of six spherical silica carriers (silicas A-F) with solutions of cobalt and zirconium compounds. At each impregnation step a quantity of solution was used of which the volume substantially corresponded to the pore volume of the carrier concerned. After each impregnation step the solvent was removed by
35 heating and the material was calcined at 500 °C. After the final

calcination the compositions were activated in hydrogen as follows: catalysts 1-3, 6, 8 and 9 at 260 °C and catalysts 4, 5 and 7 at 250 °C. Catalysts 1-9 were prepared as follows.

Catalysts 1, 2, 3, 6, 8 and 9

5 One-step or multi-step impregnation of a silica carrier with a solution of zirconium tetra-n-propoxide in a mixture of n-propanol, toluene and acetyl acetone, followed by one-step
10 impregnation of the zirconium-loaded carrier with an aqueous solution of cobalt nitrate. In the preparation of catalysts 1 and 3, the zirconium impregnation was carried out in three steps; catalysts 6, 8 and 9 were prepared via two-step zirconium
15 impregnation; in the preparation of catalyst 2, zirconium impregnation took place in one step.

Catalysts 4, 5 and 7

15 One-step impregnation of a silica carrier with an aqueous solution of cobalt nitrate, followed by one-step impregnation of the cobalt-loaded carrier with an aqueous solution of zirconium nitrate.

Further particulars of catalysts 1-9 are shown in Table I.

20 Catalysts 1-9 were used in nine experiments (experiments 1-9) in the preparation of hydrocarbons from a mixture of carbon monoxide and hydrogen having an H_2/CO molar ratio of 2. The experiments were carried out at a pressure of 20 bar in a reactor in which there was a fixed catalyst bed. The other
25 conditions under which these experiments were carried out, together with the results of the experiments, are shown in Table II.

Of the experiments shown in Table II, only experiments 7-9 are experiments according to the invention. In these experiments
30 the catalyst bed satisfied the relationship $10^6 > S_e^2 \times S_i > 2.5 \times 10^4$ and a high C_5^+ selectivity was achieved. Experiments 1-6 come outside the scope of the invention. They are included in the patent application for purposes of comparison. In these experiments using a catalyst bed satisfying
35 $S_e^2 \times S_i < 2.5 \times 10^4$, a relatively low C_5^+ selectivity was observed.

TABLE I

Catalyst No.	1	2	3	4	5	6	7	8	9
Silica carrier	A	B	B	A	C	C	D	E	F
Zr load, ppw Zr/100 ppw SiO ₂	18	6	18	0.9	0.9	12	0.9	12	12
Co load, mg Co/ml catalyst	41	33	101	36	93	102	97	94	40
S _i , m ² /ml	28	32	30	29	107	104	100	97	31
S _e , cm ² /ml	15	26	26	15	14	14	26	24	35
S _e ² x S _i	6300	21632	20280	6525	20972	20384	67600	55872	40176

TABLE II

Experiment No.	1	2	3	4	5	6	7	8	9
Catalyst No.	1	2	3	4	5	6	7	8	9
Temperature, °C	240	227	220	240	225	215	215	210	220
Space velocity, NL.l ⁻¹ .hour ⁻¹	1000	900	1000	1000	900	900	900	900	900
Conversion of the H ₂ /CO mixture, % by volume	57	60	53	52	64	65	61	58	63
C ₁ ⁺ production, g.l ⁻¹ .hour ⁻¹	108	101	103	100	109	110	103	101	110
C ₅ ⁺ selectivity, % by weight	60	72	64	52	64	70	76	79	78

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C L A I M S

1. Process for the preparation of hydrocarbons by catalytic reaction of carbon monoxide with hydrogen, characterized in that a mixture of carbon monoxide and hydrogen is contacted at elevated temperature and pressure with a catalyst which contains 3-60 parts
 5 by weight of cobalt and 0.1-100 parts by weight of at least one other metal selected from zirconium, titanium and chromium per 100 parts by weight of silica, alumina or silica-alumina, the catalyst being prepared by kneading and/or impregnation, in that the catalyst is present in the form of a fixed bed and in that the
 10 catalyst bed has an external surface area (S_e) between 5 and 70 cm^2/ml and an internal surface (S_i) between 10 and 400 m^2/ml such as to satisfy the relationship $10^6 > S_e^2 \times S_i > 2.5 \times 10^4$.

2. Process as claimed in claim 1, characterized in that the catalyst bed has an S_e between 10 and 50 cm^2/ml and an S_i between
 15 15 and 200 m^2/ml such as to satisfy the relationship $2.5 \times 10^5 > S_e^2 \times S_i > 3 \times 10^4$.

3. Process as claimed in claim 1 or 2, characterized in that the catalyst satisfies the relationship

$$(3 + 4 R) > \frac{L}{S_i} > (0.3 + 0.4 R), \text{ wherein}$$

20 L = the total quantity of cobalt present on the catalyst, expressed in mg of Co/ml,

S_i = the internal surface area of the catalyst, expressed in m^2/ml , and

25 R = the weight ratio between the quantity of cobalt applied to the catalyst by kneading and the total quantity of cobalt present on the catalyst.

4. Process as claimed in any one of claims 1-3, characterized in that the catalyst contains 15-50 parts by weight of cobalt per 100 parts by weight of carrier and either 0.1-5 parts by weight of the
 30 other metal if in the preparation first cobalt and then the other

metal is applied or 5-40 parts by weight of the other metal if in the preparation first the other metal and then cobalt is applied.

- 5 5. Process as claimed in any one of claims 1-4, characterized in that the catalyst contains zirconium as the other metal and silica as carrier.
6. Process as claimed in any one of claims 1-5, characterized in that it is carried out at a temperature of 125-350 °C and a pressure of 5-100 bar.
- 10 7. Process as claimed in any one of claims 1-6, characterized in that the H_2/CO mixture has an H_2/CO molar ratio between 1.75 and 2.25.
- 15 8. Process as claimed in any one of claims 1-7, characterized in that in order to prepare middle distillates from the product prepared over the cobalt catalyst, at least that portion of which the initial boiling point is above the final boiling point of the heaviest middle distillate desired as end product is subjected to a hydrocracking treatment by contacting it at elevated temperature and pressure with a catalyst containing one or more noble metals of Group VIII on a carrier.
- 20 9. Process as claimed in claim 8, characterized in that in the hydrocracking treatment a catalyst is used containing 0.1-2% by weight of one or more noble metals of Group VIII.
- 25 10. Process as claimed in any one of claims 8-9, characterized in that in the hydrocracking treatment a catalyst is used containing platinum or palladium as noble metal of Group VIII and silica-alumina as carrier.